1 The classical Schrödinger Equation

The Schrödinger Equation is ***the*** fundamental equation of Quantum Mechanics, which describes in general the time- and coordinate dependent characteristics in a chosen frame of the evolution of microscopic particles, e.g. moving electrons in the shell or cloud around an atomic nuclei. It is not possible to derive the Schrödinger Equation from first principles in a classical way, i.e. it cannot be derived from, e.g. a master equation or as a solution of a partial differential equation. Nevertheless the simplest form of the Schrödinger Equation –time independent and one-dimensional– can be derived somewhat heuristically with a few assumptions starting from the classical wave equation:

$$\frac{\partial^2\psi}{\partial t^2} = c^2 \cdot \frac{\partial^2\psi}{\partial x^2}\,. \tag{1.1}$$

Let us now assume, that the still unknown Schrödinger Equation has some form like Equation 1.1, because we may think, that if its a kind of equation describing electrons as waves according to the particle-wave duality, it may somehow resemble Equation 1.1. Therefore we set an equation of the form

$$\frac{\partial^2\psi}{\partial t^2} = \Theta \cdot \frac{\partial^2\psi}{\partial x^2}\,, \tag{1.2}$$

where Θ is a constant to be determined. The solution to the partial differential equation Equation 1.2 is obtained by assuming that ψ is a function, which differentiated two times, does not change –so to say– its form in principle. Functions of that kind are the classical trigonometric functions $\sin(x)$, $\cos(x)$, and the exponential function e^x, as these functions always repeat themselves except a constant through any number of differentiation. We may now write the solution to Equation 1.2 in the form

$$\psi = A \cdot \sin(\omega t - kx)\,, \tag{1.3}$$

where ω is the angular frequency defined as

$$\omega = 2\pi\nu\,, \tag{1.4}$$

and k is the wave number defined as

$$k = \frac{\omega}{v} \tag{1.5}$$

conforming to classical physics. ν is the frequency of the wave and

$$v = \lambda \cdot \nu \tag{1.6}$$

its velocity. λ is the wave-length. A is the amplitude, t is the time and x the horizontal dimension or coordinate respectively.
If we differentiate Equation 1.3 two times with respect to ∂x and ∂t we arrive at:

$$\frac{\partial}{\partial x}(A \cdot \sin(\omega t - kx)) = k \cdot A \cdot \cos(\omega t - kx)$$

$$\frac{\partial^2}{\partial x^2}(k \cdot A \cdot \cos(\omega t - kx)) = -k^2 \cdot A \cdot \sin(\omega t - kx) \tag{1.7a}$$

$$\frac{\partial}{\partial t}(A \cdot \sin(\omega t - kx)) = \omega \cdot A \cdot \cos(\omega t - kx)$$

$$\frac{\partial^2}{\partial t^2}(\omega \cdot A \cdot \cos(\omega t - kx)) = -\omega^2 \cdot A \cdot \sin(\omega t - kx)\,. \tag{1.7b}$$

But Equation 1.7a and Equation 1.7b are simply

$$\frac{\partial^2 \psi}{\partial x^2} = -\,k^2 \cdot A \cdot \sin(\omega t - kx) = -k^2 \cdot \psi \tag{1.8a}$$

$$\frac{\partial^2 \psi}{\partial t^2} = -\,\omega^2 \cdot A \cdot \sin(\omega t - kx) = -\omega^2 \cdot \psi\,. \tag{1.8b}$$

If we now insert Equation 1.8a and Equation 1.8b into Equation 1.2 we get

$$-\omega^2 \cdot \psi = \Theta \cdot -k^2 \cdot \psi \tag{1.9}$$

from which we see that

$$\Theta = \frac{\omega^2}{k^2}\,. \tag{1.10}$$

Our Equation 1.2 then reads

$$\frac{\partial^2 \psi}{\partial t^2} = \frac{\omega^2}{k^2} \cdot \frac{\partial^2 \psi}{\partial x^2} \tag{1.11}$$

as a first result.
We now make use of classical results of early scientific research in Quantum Mechanics, namely of the de-Broglie wave-length, which states that the product of the wavelength λ of the "particle-wave" with the impulse p of the particle is a constant, i.e. it is quantized. This is written as

$$\lambda = \frac{h}{p} \tag{1.12}$$

where h is a fundamental constant, called the PLANCK constant and p is the impulse of the wave-like particle as mentioned before. We make further use of a famous equation for the kinetic energy $\mathscr{E}$ of a particle according to

$$\mathscr{E} = \frac{1}{2} \cdot mv^2 \tag{1.13}$$

which we write as

$$\mathscr{E} = \frac{p^2}{2m}\,, \tag{1.14}$$

where we have used the relation to compute the impulse of a particle according to

$$p = m \cdot v\,. \tag{1.15}$$

The total energy E of the particle is given as the sum of its kinetic energy $\mathscr{E}$ and its potential energy V. Therefore Equation 1.14 is written in the form

$$(\mathscr{E} + V) = \frac{p^2}{2m}\,. \tag{1.16}$$

We now introduce Equation 1.4, Equation 1.5, and Equation 1.6 in Equation 1.10, which yields

$$\begin{aligned} \frac{\omega^2}{k^2} &= \frac{4\pi\nu^2}{\frac{4\pi^2\nu^2}{\lambda^2\cdot\nu^2}} \\ &= \lambda^2 \cdot \nu^2\,, \end{aligned}$$

which in return gives, with Equation 1.12 and Equation 1.16

$$\begin{aligned} \lambda^2 \cdot \nu^2 &= \frac{h^2}{p^2} \cdot \nu^2 \\ &= \frac{\hbar^2 \cdot 4\pi^2}{2m \cdot (\mathscr{E} + V)}\,, \end{aligned} \tag{1.17}$$

where we have introduced $\hbar = \frac{h}{2\pi}$, called the reduced PLANCK constant. Equation 1.11 therefore reads

$$\frac{\partial^2\psi}{\partial t^2} = \frac{\hbar^2 \cdot 4\pi^2}{2m \cdot (\mathscr{E} + V)} \cdot \nu^2 \cdot \frac{\partial^2\psi}{\partial x^2} \tag{1.18}$$

As we deal with a time independent SCHRÖDINGER Equation, we substitute the term $\frac{\partial^2\psi}{\partial t^2}$ with Equation 1.8b which gives

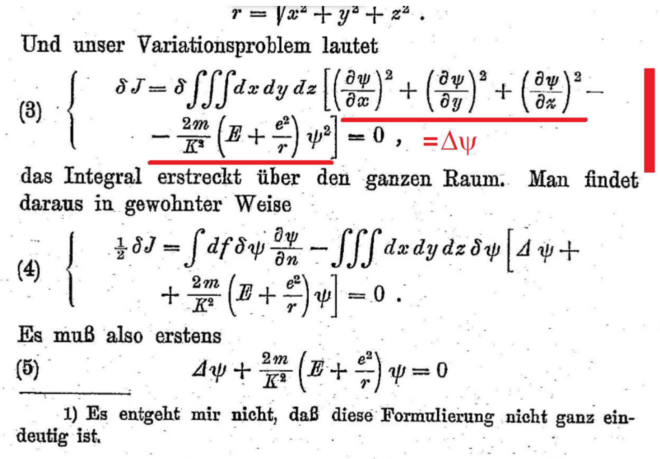
$$-\omega^2 \cdot \psi = \frac{\hbar^2 \cdot 4\pi^2}{2m \cdot (\mathscr{E} + V)} \cdot \nu^2 \cdot \frac{\partial^2\psi}{\partial x^2}\,. \tag{1.19}$$

But ω^2 on the l.h.s. of Equation 1.19 is just the same as $4\pi^2 \cdot \nu^2$ on the r.h.s. of Equation 1.19 and therefore cancels itself out. We finally rearrange Equation 1.19

$$\boxed{(\mathscr{E} + V) \cdot \psi = -\frac{\hbar^2}{2m} \cdot \frac{\partial^2\psi}{\partial x^2}} \tag{1.20}$$

to have the standard time independent SCHRÖDINGER Equation in one dimension. In Figure 1.1 is shown the original formula taken from E. SCHRÖDINGER:

"Quantisierung als Eigenwertproblem I" in *Annalen der Physik*, Vol. 79 (1926), p. 361–376.



$$r = \sqrt{x^2 + y^2 + z^2}\,.$$

Und unser Variationsproblem lautet

$$(3)\quad \left\{\begin{aligned} \delta J = \delta \iiint dx\,dy\,dz \Big[\Big(\frac{\partial\psi}{\partial x}\Big)^2 + \Big(\frac{\partial\psi}{\partial y}\Big)^2 + \Big(\frac{\partial\psi}{\partial z}\Big)^2 - \\ - \frac{2m}{K^2}\Big(E + \frac{e^2}{r}\Big)\psi^2\Big] = 0\,, \end{aligned}\right.$$

das Integral erstreckt über den ganzen Raum. Man findet daraus in gewohnter Weise

$$(4)\quad \left\{\begin{aligned} \tfrac{1}{2}\delta J = \int df\,\delta\psi\frac{\partial\psi}{\partial n} - \iiint dx\,dy\,dz\,\delta\psi\Big[\Delta\psi + \\ + \frac{2m}{K^2}\Big(E + \frac{e^2}{r}\Big)\psi\Big] = 0\,. \end{aligned}\right.$$

Es muß also erstens

$$(5)\qquad \Delta\psi + \frac{2m}{K^2}\Big(E + \frac{e^2}{r}\Big)\psi = 0$$

1) Es entgeht mir nicht, daß diese Formulierung nicht ganz eindeutig ist.

Figure 1.1: Original illustration of the SCHRÖDINGER Equation

Δ is the LAPLACE operator and is defined for a function f (or ψ) depending on the three variables x, y, and z in a cartesian coordinate system as

$$\Delta f = \frac{\partial^2 f}{\partial x^2} + \frac{\partial^2 f}{\partial y^2} + \frac{\partial^2 f}{\partial z^2}\,. \tag{1.21}$$

The formula (5) in Figure 1.1 can be written with the help of Equation 1.21 in the form

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{2m}{K^2}\cdot\left(\mathscr{E} + \frac{e^2}{r}\right)\cdot\psi = 0 \tag{1.22}$$

which is, when rearranged, identical to Equation 1.20. Note, that $\frac{e^2}{r} = V$ is the potential energy of an electron moving in an electrostatic field.[1] In Figure 1.2 the constant K is determined, which shows to be $K = \hbar = \frac{h}{2\pi}$, i.e. the reduced PLANCK constant that we introduced in Equation 1.17.

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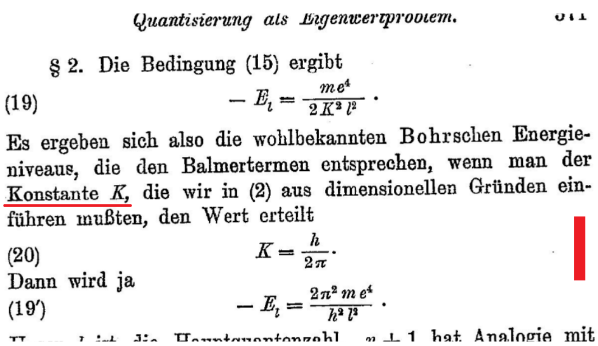
[1] The term $\frac{e^2}{r}$ stems from the famous COULOMB's law, which states that the magnitude of the electrostatic force of attraction or repulsion between two electrons e is directly proportional (i) to the product of the magnitudes of charges and (ii) inversely proportional to the square of the distance r between them.



Quantisierung als Eigenwertproblem.

§ 2. Die Bedingung (15) ergibt

$$-E_l = \frac{me^4}{2K^2 l^2}\,. \tag{19}$$

Es ergeben sich also die wohlbekannten Bohrschen Energieniveaus, die den Balmertermen entsprechen, wenn man der Konstante K, die wir in (2) aus dimensionellen Gründen einführen mußten, den Wert erteilt

$$K = \frac{h}{2\pi}. \tag{20}$$

Dann wird ja

$$-E_l = \frac{2\pi^2 m e^4}{h^2 l^2}\,. \tag{19'}$$

Figure 1.2: Determination of the constant K, shown in Figure 1.1